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Physical Properties and Composition Detection of Biodiesel-diesel Fuel Blends

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Abstract. *Biodiesel is an oxygenated, sulfur-free, biodegradable, non-toxic, and environmentally friendly alternative diesel fuel. Biodiesel can be derived from renewable resources, such as vegetable oils, animal fats, and waste restaurant greases. One of the attractive characteristics of biodiesel is that its use does not require any significant modifications to the diesel engine, so the engine does not have to be dedicated for biodiesel. However, due to its different properties, biodiesel will cause some changes in the engine performance and emissions including lower power and higher oxides of nitrogen. Biodiesel can be blended in any proportion with petroleum-based diesel fuel and the impact of the changes is usually proportional to the fraction of biodiesel being used. If the biodiesel-diesel fuel blend level were known, these changes could be eliminated by the engine's electronic control system. The objective of this study was the investigation of the effect of biodiesel blend level on density, speed of sound, and isentropic bulk modulus at higher pressures, and at 20 °C and 40 °C. Also, blend detection with a commercial fuel composition sensor, and the effect of temperature, water, and alcohol on this detection was investigated.*

Keywords. Esters, Biodiesel, Diesel Fuel, Physical Properties, Density, Speed of Sound, Isentropic Bulk Modulus, Compressibility, Fuel Injection Timing, Blend Detection, Fuel Composition Sensor.

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Introduction

Limited energy resources and increasingly strict emission regulations have motivated an intense search for alternative transportation fuels over the last three decades. Biodiesel is an oxygenated, sulfur-free, biodegradable, non-toxic, and environmentally friendly alternative diesel fuel. Biodiesel is defined as the alkyl monoesters of fatty acids from renewable resources, such as vegetable oils, animal fats, and waste restaurant greases. One of the attractive characteristics of biodiesel is that its use does not require any significant modifications to the diesel engine, so the engine does not have to be dedicated for biodiesel. However, similar to alcohol fuels, biodiesel has a lower energy content and different physical properties than diesel fuels (Tat and Van Gerpen, 1999; Tat and Van Gerpen, 2000a; and Tat et al., 2000b). Due to its different properties, biodiesel will cause some changes in the engine performance and emissions including lower power and higher oxides of nitrogen. Biodiesel can be blended in any proportion with petroleum-based diesel fuel and the impact of the changes is usually proportional to the fraction of biodiesel being used. If the biodiesel-diesel fuel blend level is known, these changes can be eliminated by the engine's electronic control system by either injecting more fuel or adjusting the fuel injection timing. This will require advanced knowledge of biodiesel fuel properties, their impact on engine performance and emissions, blend characteristics of biodiesel with No. 1 (winter blend) and No. 2 diesel fuel, and blend detection.

The objective of this study was the investigation of the effect of blending biodiesel with No. 1 and No. 2 diesel fuel on density, speed of sound, and isentropic bulk modulus at higher pressures, and at 20 °C and 40 °C. Blend detection with a commercial fuel composition sensor, and the effect of temperature, water, and alcohol on this detection was also investigated. In this study, the distribution of the physical properties of the blends with No. 1 and No. 2 diesel fuel are presented and the blending effect on these properties was investigated at 20 °C both for No. 1 and No. 2 diesel fuels. Regression equations for the effect of temperature, pressure, and blend level were also obtained.

A Ford Flexible Fuel Composition Sensor (Ford Part No. YL5A-9C044-AA) was described in an earlier paper for measuring biodiesel composition in biodiesel-diesel fuel blends (Tat and Van Gerpen, 2001). This sensor was originally designed to detect the methanol or ethanol composition in methanol/ethanol-gasoline blends. This paper presents the results of further testing of the sensor to identify the impact of temperature, water, and alcohol on the detection.

Materials and Methods

Density and speed of sound were measured in 100% biodiesel (soy methyl ester) made by Iowa State University and commercial grade No. 1 and No. 2 diesel fuels. Also, blends of 20, 50, and 75% biodiesel with the No. 1 and No. 2 diesel fuels were prepared and measured from atmospheric pressure to 32.46 MPa and at temperatures of 20 and 40 °C. The isentropic bulk modulus, which is the inverse of compressibility, was also calculated at each pressure and temperature level using Equation 1 (Boelhouwer, 1967; Rolling and Vogt, 1960).

$$\beta = c^2 \times \rho \quad (1)$$

where β is the isentropic bulk modulus in Pascal, c is the speed of sound in the sample in m/s, and ρ is the density in kg/m³.

Detailed information about the physical and the chemical properties of the biodiesel and the commercial grades of No. 1 and No. 2 diesel fuels are given in Table A1 of the appendix.

The ultrasonic pulse echo technique was used to measure the speed of sound in the fuel samples (McClements and Povey, 1992; Kuo, 1971; and McClements and Povey, 1988). A Panametrics Model 5072 PR general purpose ultrasonic pulser/receiver and a Panametrics 10 MHz videoscanner immersion transducer (Waltham, MA) were used. A pressure vessel with a piston and cylinder assembly for raising the pressure was fabricated and the ultrasonic transducer was located at the bottom of the vessel. Signals were captured with a Hewlett Packard Model 54601A 100 MHz, 4 channel digital oscilloscope (Colorado Springs, CO). System pressure was measured using a Sensotec Model 2 Z/1108-04Z9 pressure transducer (Columbus, OH). To obtain elevated temperatures the entire pressure vessel was submerged in a temperature controlled bath. Detailed information about the pressure vessel and equipment was given in Tat et al. (2000b) and Tat and Van Gerpen (2002).

The density was initially measured at atmospheric pressure and temperatures of 20 °C and 40 °C using a modified specific gravity balance (Troemner Company, Philadelphia, PA). A copper graduated cylinder and a small constant temperature bath were adapted to the balance. The temperature change in the graduated cylinder was monitored with a thermocouple. A detailed explanation of this measurement was given in Tat and Van Gerpen (2000a). Four measurements were taken at each temperature level and repeated two times. Therefore, at atmospheric pressure, 8 measurements were obtained. The balance was calibrated with distilled water to 1.0000 at 15.5 °C before the measurements. At higher pressures, the density was calculated using the volume change of the pressure vessel at each pressure level for two fillings and with 2 measurements at each temperature level.

Ford Motor Co. donated one dielectric fuel composition sensor that was originally designed for detection of the methanol concentration in methanol-gasoline blends. The sensor is shown in Figure 1. The sensor gives a square wave output with a frequency that is proportional to the blend composition and the duration of the high portion of the wave is proportional to the temperature of the blend. This sensor had been tested before for biodiesel blend response and the data are given in Figure 2 (Tat and Van Gerpen, 2002). A HP 5335 A Universal Counter was used for counting the average frequency over a three minute period and the measurements were repeated three times. A 12 Volt power supply provided power to the sensor, and a pull-up resistor was connected from the output of the sensor to 12V. More information about the sensor and the measurement are given in Tat and Van Gerpen (2002).

Soy methyl ester biodiesel and the commercial No. 2 diesel fuel were tested for the effect of temperature on the sensor response. The biodiesel was also tested for the effect of methanol and water content. The sensor was connected to a Holley electric fuel pump and a 500 ml fuel storage flask, which was submerged in a Haake A81 temperature-controlled heating bath.

To investigate the effect of water, soy methyl ester biodiesel fuel samples were tested at three water levels. The first sample was called *dry* biodiesel because it was boiled under vacuum for 20 minutes to evaporate any water and then it was tested immediately after. The second sample was called *normal* and had been allowed to come to equilibrium with the ambient temperature and humidity. The last sample was *saturated* with water. To prepare this sample, soy methyl ester was mixed with distilled water for 20 minutes at room temperature and then settled overnight to separate the water. It was tested the next day.

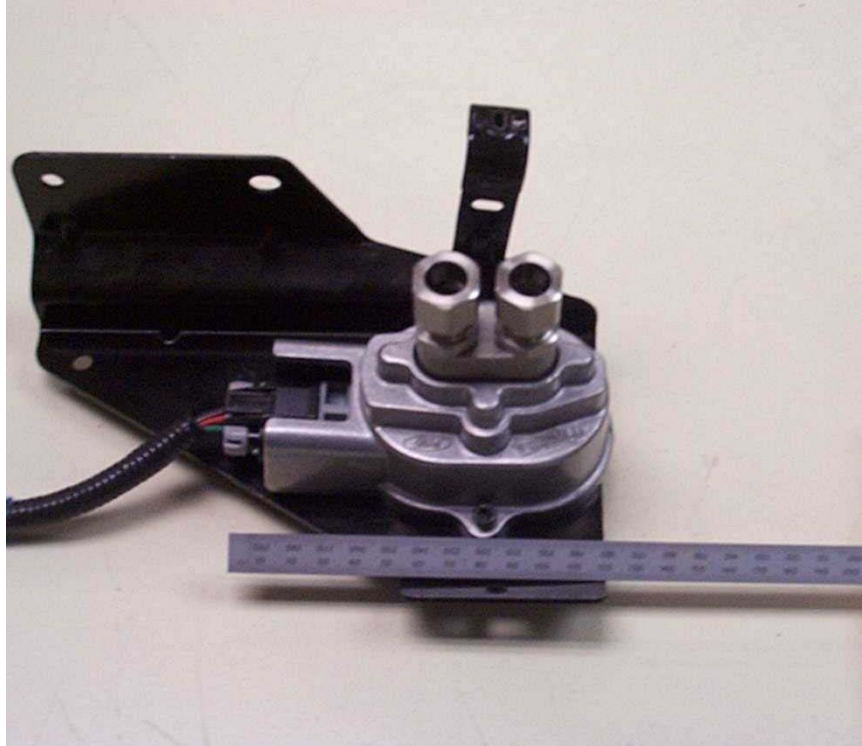


Figure 1. Flexible Fuel Composition Sensor (Ford Part No. YL5A-9C044-AA).

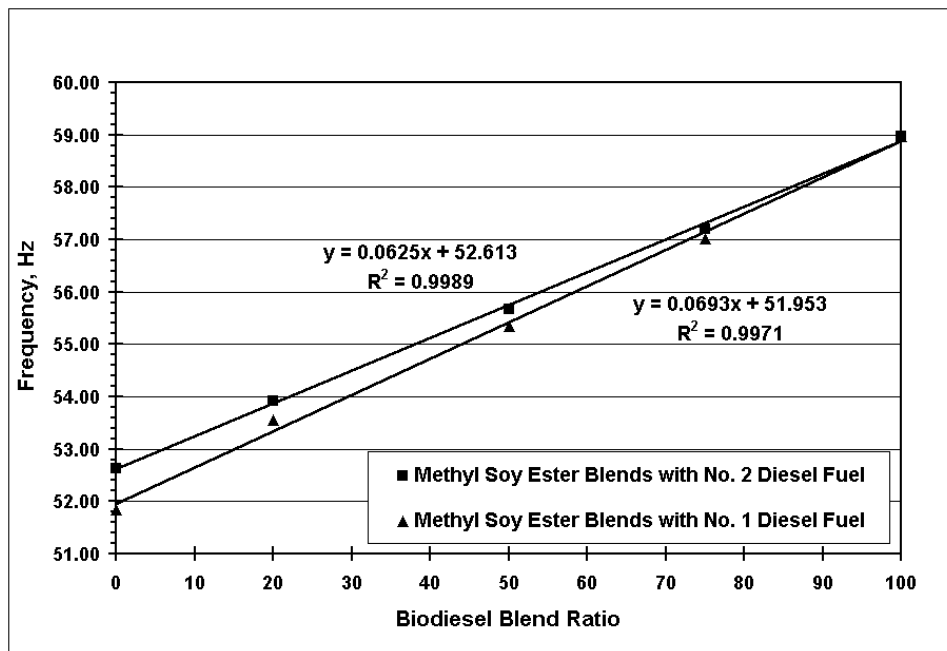


Figure 2. Soy Methyl Ester Blends with No. 2 and No. 1 Diesel Fuel (Tat and Van Gerpen, 2002).

Results

The density, speed of sound, and the isentropic bulk modulus of the fuel samples showed approximately linear relationships with pressure at the two temperature levels, 20 and 40 °C. A polynomial that was linear in temperature, pressure, and blend percentage was used to fit the density and isentropic bulk modulus data. This equation is shown in Equation 2. A more complex three variable polynomial was used to fit the speed of sound data for the blends with both No. 1 and No. 2 diesel fuel. The general form of this equation is shown in Equation 3.

$$y = C_1T + C_2P + C_3\% + C_4 \quad (2)$$

$$y = C_1T + C_2P + C_3\% + C_4TP + C_5P\% + C_6P^2 + C_7\%^2 + C_8 \quad (3)$$

where y is the density, speed of sound, or the isentropic bulk modulus of the blends of No.1 and No. 2 diesel fuel with biodiesel fuel, T is the temperature in °C, P is the pressure in MPa, % is the biodiesel percentage in the blend, and $C_i, i=1,8$ are the regression constants given in Tables 1-3. The R^2 values and the standard errors for y calculated by an Excel spread sheet are also shown in the Tables.

The density, speed of sound, and the isentropic bulk modulus of the No. 2 diesel fuel blends are presented in Figures 3, 4, and 5, respectively at 20 °C. In Figures 3 and 4, the points are the averaged measured values at each pressure level and the lines are the regression results calculated using Equations 2 and 3. Error bars represent the 90% confidence intervals. As can be observed from the figures, the density and the isentropic bulk modulus show very linear behavior with blend percentage at each pressure level. The speed of sound data were approximately linear with biodiesel percentage, but it was necessary to use a higher degree polynomial to increase the regression accuracy. The density, speed of sound, and isentropic bulk modulus data also showed very linear behavior with pressure. Results were similar at 40 °C to those at 20 °C.

Figures 6-8 show the effect of temperature, methanol, and water content on the sensor response. Temperature slightly increased the output of the sensor for both the biodiesel and No. 2 diesel fuels. However, the increment was small. Methanol content in the biodiesel fuel led to a maximum of 1.5% increase in the frequency output when the methanol content was 1%. This level of methanol is above the amount that would be allowed by the flash point specification for biodiesel (Van Gerpen, et al., 1997). As shown in Figure 7, water content also had almost no effect on the sensor output.

Table 1. Density regression constants.

Samples	$C_1 \times 10^4$	$C_2 \times 10^4$	$C_3 \times 10^4$	$C_4 \times 10$	R^2	$Se_y \times 10^4$
No. 2 Diesel Fuel Blends	2.6324	5.8574	-6.5302	8.6671	0.9983	5.5
No. 1 Diesel Fuel Blends	5.9030	6.1040	-6.5757	8.3318	0.9991	7.2
Density (gr/cm ³) = $C_1 \times T(^{\circ}C) + C_2 \times P(MPa) + C_3 \times \%(Biodiesel \text{ Percentage}) + C_4$						

Table 2(a). Speed of sound regression constants.

Samples	C ₁	C ₂	C ₃ ×10	C ₄ ×10 ²	C ₅ ×10 ³	C ₆ ×10 ²	C ₇ ×10 ⁴	C ₈ ×10 ⁻³
No. 2 Blends	-3.5972	4.6849	2.3682	1.4412	-3.9664	-1.6236	8.8429	1.4570
No. 1 Blends	-3.7043	5.0232	6.5479	1.4958	-6.9146	-1.7425	11.8120	1.4147

Speed of Sound (m/s) = C₁×T(°C) + C₂×P(MPa) + C₃×%(Biodiesel Percentage) + C₄×T×P + C₅×P×% + C₆×P² + C₇×%² + C₈

Table 2(b). R² values and Se_y values of speed of sound value.

Samples	R ²	Se _y ×10 ⁴
No. 2 Diesel Fuel Blends	0.9989	2.0
No. 1 Diesel Fuel Blends	0.9990	2.1

Table 3. Isentropic bulk modulus regression constants.

Samples	C ₁	C ₂ ×10 ⁻¹	C ₃	C ₄ ×10 ⁻³	R ²	Se _y
No. 2 Diesel Fuel Blends	1.1927	1.2170	-9.7434	1.8384	0.9985	6.8
No. 1 Diesel Fuel Blends	2.7763	1.2206	-9.6579	1.6727	0.9983	8.1

Isentropic Bulk Modulus (MPa) = C₁×T(°C) + C₂×P(MPa) + C₃×%(Biodiesel Percentage) + C₄

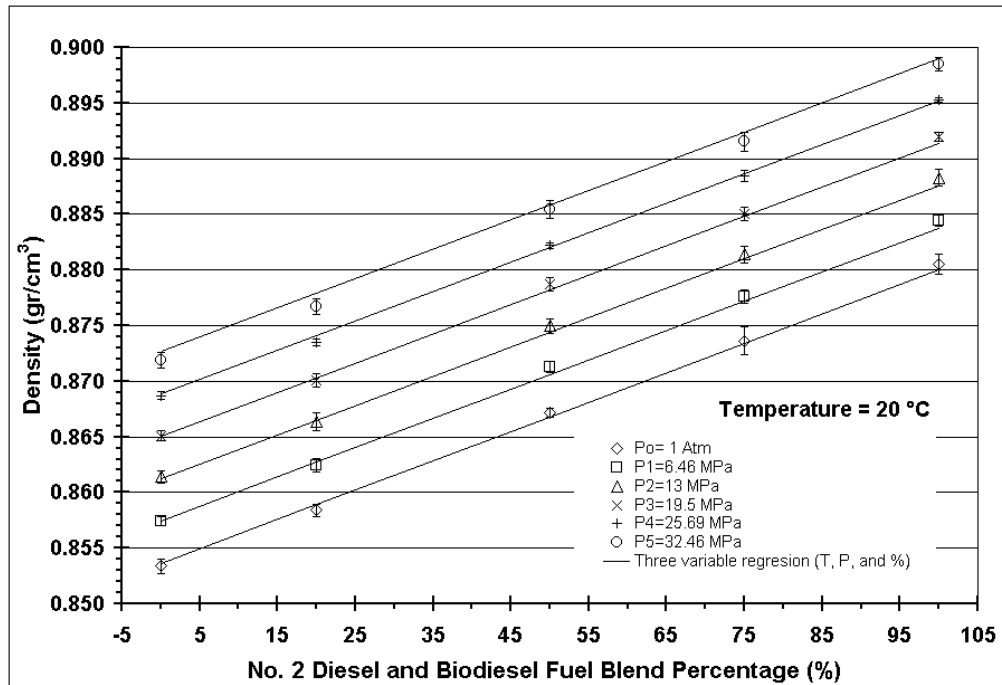


Figure 3. Density comparison between measured data and regression equation.

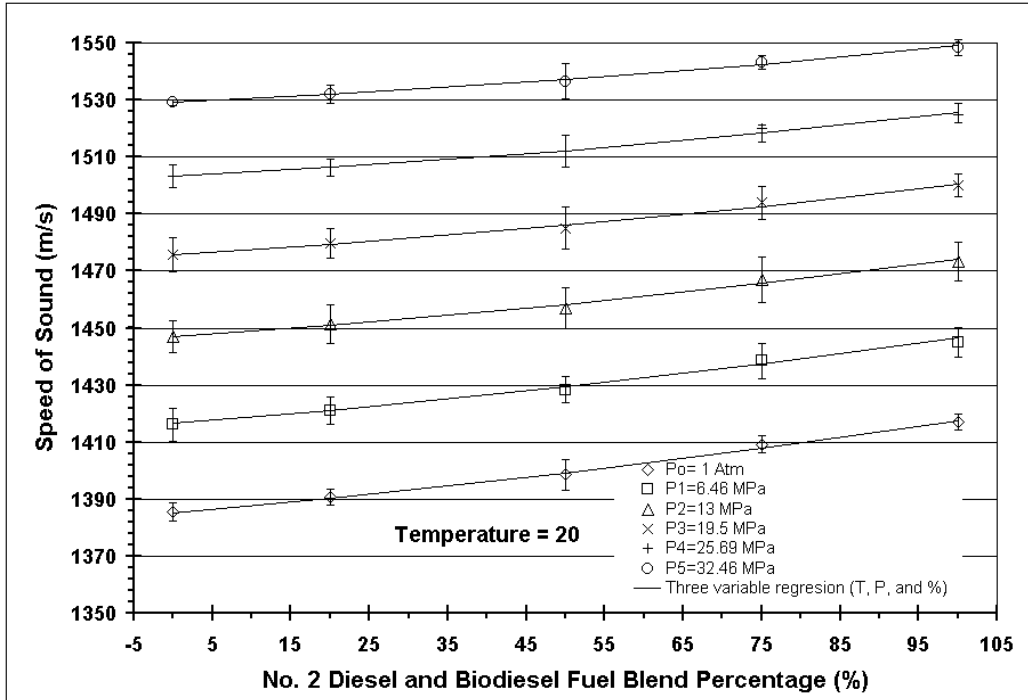


Figure 4. Speed of sound comparison between measured data and regression equation.

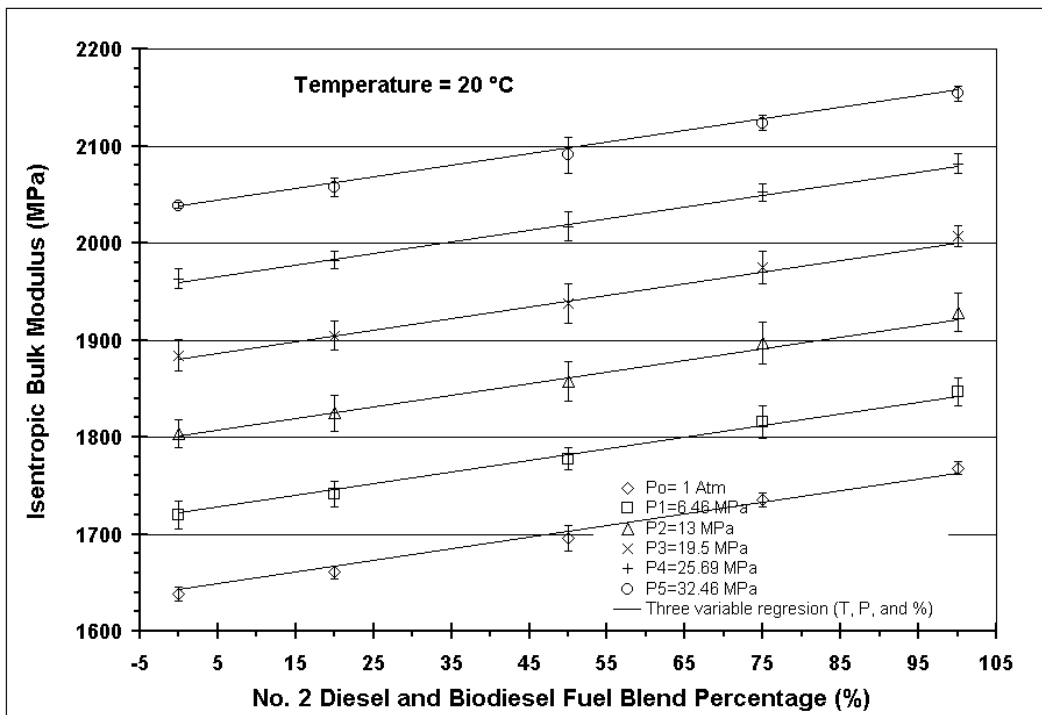


Figure 5. Isentropic bulk modulus comparison between measured data and regression equation.

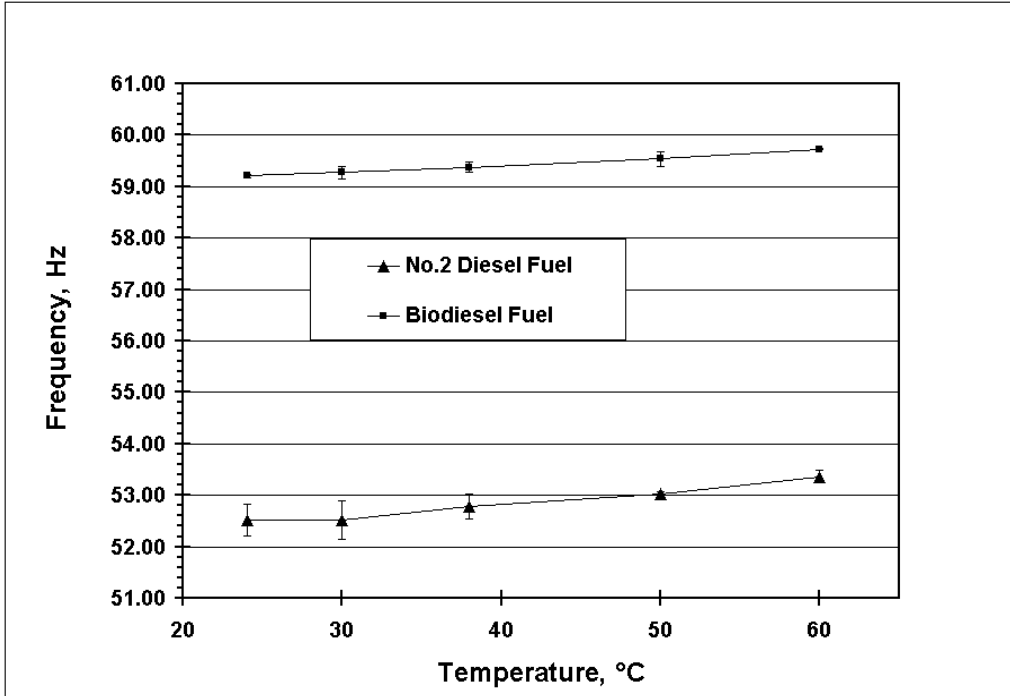


Figure 6. Temperature effect on soy methyl ester (Biodiesel) and No. 2 diesel fuel sensor output.

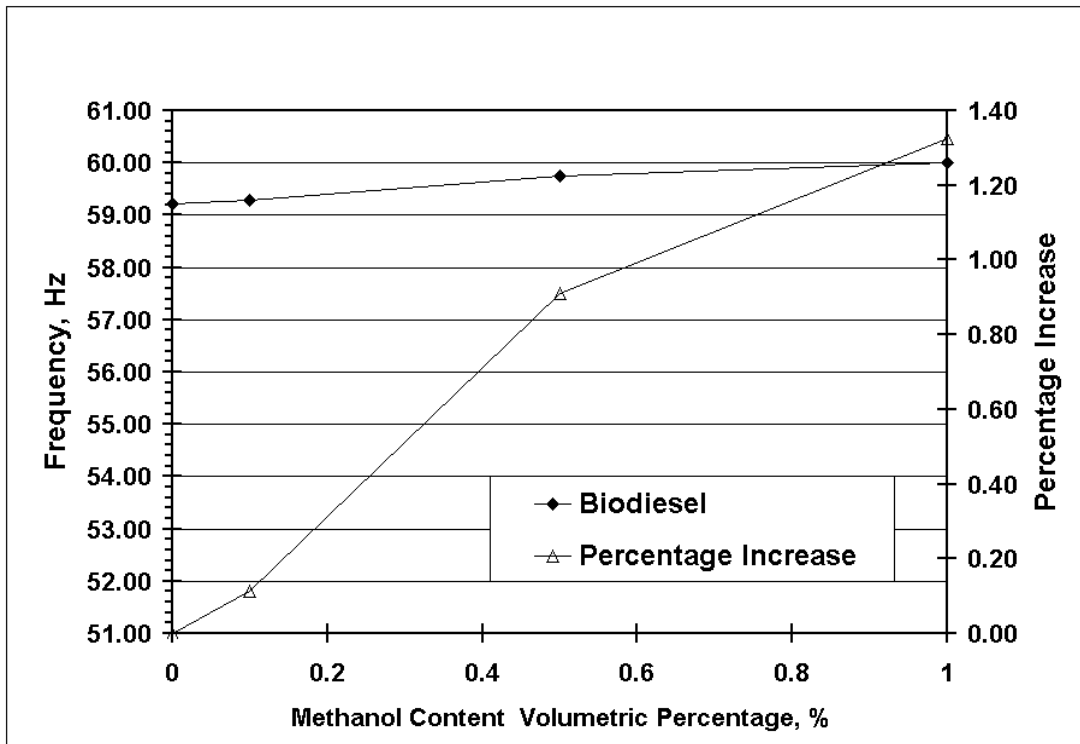


Figure 7. Methanol content effect on biodiesel sensor output.

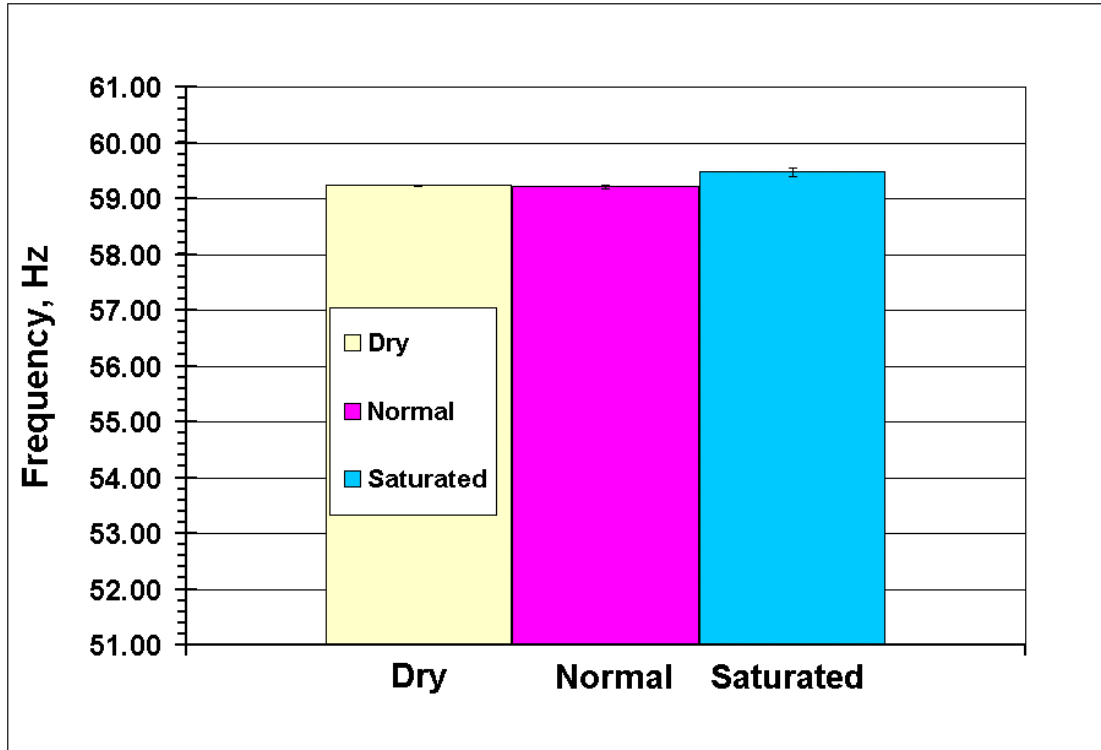


Figure 8. Water content effect on biodiesel sensor output.

Conclusions

Biodiesel-fueled vehicles can be called non-dedicated alternatively fuel vehicles because biodiesel use does not require any significant modifications to the engine, so that the engine does not have to be dedicated for biodiesel use only. It is completely soluble in commercial petroleum-based diesel fuel, so biodiesel can be used as a blend and one fuel tank can be used for storage of both fuels. This is a unique advantage compared with most other alternative fuels, because this will give users the opportunity to use the alternative fuel where and when it is available without paying any extra money for engine modifications. Many large engine and car manufacturers have included biodiesel fuel in their warranties (Korbitz, 1999). Depending on the trade-off between cost and its environmental benefits, biodiesel will be most commonly used in blends with No. 1 or No. 2 diesel fuels.

Biodiesel has different physical and chemical properties that provide its advantages over petroleum-based diesel fuel. However, these property differences can also provide disadvantages such as power loss and higher NO_x emissions. Therefore, the blending effects on the fuel properties should be known and the detection of the blend level may be required in order to provide equal power and emissions.

In this study, a linear change in the density, speed of sound, and the isentropic bulk modulus with biodiesel blend percentage has been observed. Regression equations and constants as a function of temperature, pressure, and blend fraction were given. The Ford flexible fuel sensor results showed that the sensor is not significantly affected by temperature, methanol, and water level.

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Appendix

Table A.1 The Physical and Chemical Properties of Commercial No.2 and No. 1 Diesel Fuels.

Test Property	Commercial No. 2 Diesel Fuel	Commercial No.1 Diesel Fuel	Soy Methyl Ester
Carbon (% mass)	86.70 ^a	86.83 ^a	77.10 ^e
Hydrogen (% mass)	12.71 ^a	12.72 ^a	11.81 ^e
Oxygen (% mass)	-	-	10.97 ^e
C/H Ratio	6.82	6.826	6.53
Sulfur (% mass)	0.041 ^a	0.045 ^a	<0.005 ^a
Cetane Number (ASTM D613)	42.6 ^a	45.3 ^a	51.5 ^a
Gross Heat of Combustion (kJ/kg)	45,339 ^a	45,991 ^a	39,871 ^a
Net Heat of Combustion (kJ/kg)	42,640 ^a	43,281 ^a	37,388 ^a
Specific Gravity (@21 °C)	0.8537 ^c	0.8162 ^c	0.8814 ^c
Kinematic Viscosity (cSt, @40 C)	2.8271 ^c	1.759 ^c	4.2991 ^c
Total Glycerin (%)	-	-	0.028 ^b
Free Glycerin (%)	-	-	0.000 ^b
<i>Distillation (ASTM D86, °F)^a</i>			
Initial Boiling Point	352	348	-
5%	392	373	-
10%	413	384	-
20%	440	394	-
30%	462	406	-
40%	482	416	-
50%	502	426	-
60%	522	440	-
70%	543	454	-
80%	569	474	-
90%	602	503	-
95%	630	535	-
End Point	653	580	-
Recovery (%)	98.0	98.0	-
Residue (%)	1.9	1.9	-
Loss (%)	0.1	0.1	-

^a Measured by Phoenix Chemical Laboratory Inc., Chicago IL.

^b Measured by Williams Laboratory Services, Kansas City, KS.

^c Measured in the Department of Mechanical Engineering, Iowa State University, Ames, IA.

^d Calculated using Universal Oil Products Method 375-86, Des Plaines IL.

^e Calculated from Fatty Acid Distribution.